

Physical Chemistry, CH341
Fall 2005, Prof. Shattuck

Final

Name _____

Constants: $F=96485 \text{ C/mol}$

$1 \text{ atm} = 1.013 \times 10^5 \text{ N m}^{-2}$

$1 \text{ bar} = 0.9872 \text{ atm}$

$2.303RT/F=0.0592\text{V}$

$RT/F=0.0257\text{V}$

$R=8.314(\text{you know units})$

$R=0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$

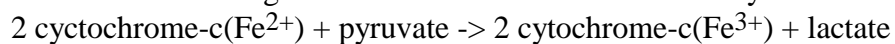
Part I

Answer 3 of the following 4 questions. If you answer more than 3 cross out the one you wish not to be graded. 12 pts. each.

1. In a first order reaction, $A \rightarrow \text{products}$, the concentration of A drops from 1M to 0.5M in 2 minutes. How long does it take for the concentration to drop from 0.5M to 0.25M?
2. Derive the integrated expression for a second-order rate law $d[P]/dt = k [A][B]$ for a reaction of stoichiometry $2A + 3B \rightarrow P$. Stop at the stage that you would need to look up the integral. [i.e. you don't need to do the difficult integral, but do the easy one]
3. Give the solubility product K_{sp} expression for HgI_2 . Write the result in terms of γ_{\pm} and the solubility, m . (That is γ_{\pm} and m should appear in your final answer.)
4. Use the Debye-Hückel law to estimate the mean ionic activity coefficient for 0.100M MgCl_2 at 298K.

Answer 3 of the following 4 questions. If you answer more than 3 cross out the one you wish not to be graded.: 17pts each.

5. For the reaction involving the reduced and oxidized forms of cytochrome-c:

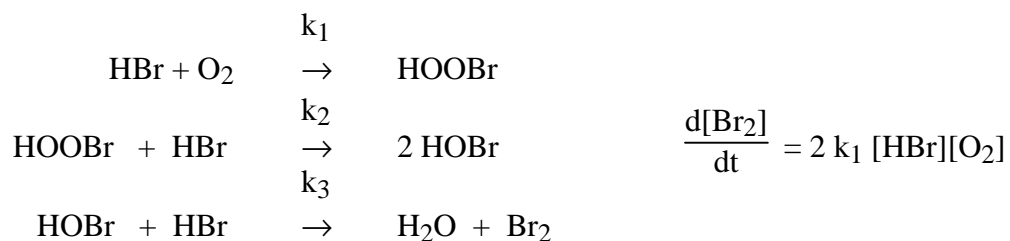


Calculate the electrochemical cell voltage at 25°C if the lactate activity is 5.00 times the pyruvate activity and the cytochrome-c(Fe³⁺) activity is 10.0 times the cytochrome-c(Fe²⁺) activity. The standard reduction potential for the pyruvate/lactate couple is -0.19V and for the cytochrome-c(Fe³⁺), (Fe²⁺) couple is 0.337V. Two electrons are transferred in the process.

6. For the reaction $\text{BeSO}_4(\text{s}) \rightarrow \text{BeO}(\text{s}) + \text{SO}_3(\text{g})$, $K_P = 3.92 \times 10^{-16}$ at 400.0 K and 1.69×10^{-8} at 600.0 K. Calculate $\Delta_r H^\circ$ for this temperature range and $\Delta_r G^\circ$ and $\Delta_r S^\circ$ at 400.0 K.

7. The partial pressure of ether over a solution of acetone in ether at 30°C is 0.713 bar at $X_{\text{ether}} = 0.800$. The partial pressure of acetone at this same concentration is 0.120 bar. Calculate the activity coefficients for ether and acetone given that $P^{\circ}_{\text{acetone}} = 0.377$ bar and $P^{\circ}_{\text{ether}} = 0.861$ bar. Use a Raoult's law standard state for both.

8. Show that the rate law is as shown below during the oxidation of HBr for the following mechanism:



Use the steady-state approximation for HOBr and HOBr.

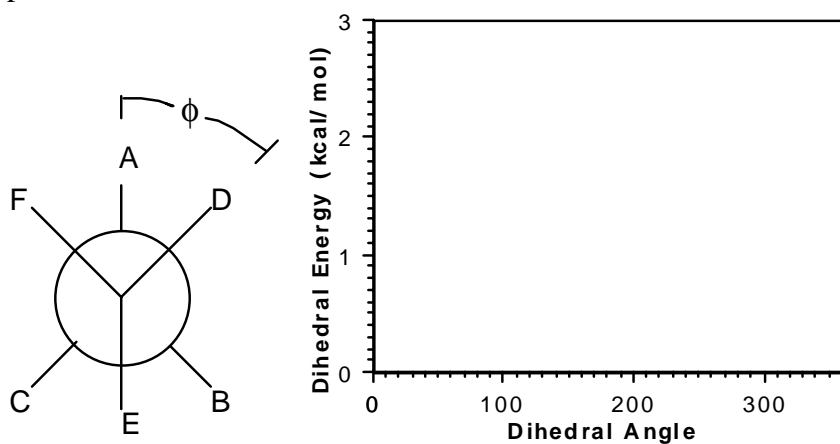
Part II

1. 8pts). Under what conditions is ΔG a good spontaneity criterion?
2. 8pts). $\left(\frac{\partial G}{\partial T}\right)_P = ?$ (for a pure substance)
3. 14pts). Three moles of N_2 occupy a volume of 3.00L at 298.K. The gas expands isothermally until it has a volume of 60.0 L. Assume N_2 is a perfect gas, and calculate the change in Gibbs Free Energy for this process.
4. 14pts) At 298.2K the vapor pressure of cyclohexane is 113. mmHg. Predict the boiling point of cyclohexane if $\Delta H_{\text{vap}}=30.1$ kJ/mol.

5. 14pts). Calculate the change in entropy for the surroundings for an isothermal irreversible expansion of one mole of ideal gas at 298.2 K from an initial pressure of 2.00 atm to a final pressure of 1.00 atm. The gas expands against a constant external pressure of 1.00 atm.

Answer 3 of the following 4 questions. If you answer more than 3 cross out the one you wish not to be graded. 17 points each.

6. (a) Sketch the molecular mechanics torsional potential for ethane, or similar molecule, on the plot below.



(b). Draw the potential energy curve for an anharmonic bond stretching potential.



7. One mole of an ideal monatomic gas, $C_v = 3/2nR$, undergoes a reversible adiabatic expansion from a volume of 1.00 L to a final volume of 2.00 L. The initial temperature is 298.2 K. Calculate the change in temperature and the change in internal energy.

8. The rate constant for the decomposition of a certain substance is $2.80 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$ at 30.0°C and $1.38 \times 10^{-2} \text{ L mol}^{-1} \text{ s}^{-1}$ at 50.0°C . Evaluate the activation energy of the reaction.

9. Show that $\left(\frac{\partial T}{\partial P}\right)_H = \frac{-1}{C_P} \left(\frac{\partial H}{\partial P}\right)_T$

[Show all your work with reasons for each step. For example: "since H is a state function" , "from the definition of heat capacity", or "dividing by dP gives the desired result". If you use a partial derivative relationship from appendix 1, rather than deriving the relationship, be sure to so state.]